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(21) International Application Number: PCT/CA90/00006 (22) International Filing Date: 2 January 1990 (02.01.90) (71) Applicant: GUERTIN BROS. COATINGS AND SEALANTS, LTD. [CA/CA]; 50 Panet Road, Winnipeg, Manitoba R2J 0R9 (CA). (72) Inventor: CHAN, Paul, Shaü, Lung ; 66 Lafayette Bay, Winnipeg, Manitoba R3T 3J8 (CA). (74) Agent: FETHERSTONHAUGH & CO.; 4, place Ville-Marie, Montréal, Québec H3B 2E7 (CA). (81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).		Published <i>With international search report.</i>
(54) Title: NCO-FREE RESINS USEFUL AS A SUBSTITUTE FOR POLYURETHANES (57) Abstract Compositions obtained by curing an acetoacetylated polymer poly(meth)acrylic or polyester-based resin and an NCO-free urethane polymer having vinylic end groups is disclosed.		

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Description**NCO-Free Resins Useful As a Substitute
for Polyurethanes**Technical Field

5 The present invention relates to NCO-free resins and coatings possessing the outstanding performance characteristics of polyurethanes.

Background Art

10 For the past several decades, urethane coatings, blocked urethanes, etc. have been very successfully used as polymers for coating and engineering polymers. They have been formulated to achieve outstanding results for the industry.

15 Most commonly, urethanes are prepared by a reaction in which free isocyanates (NCO) are reacted with various other groups in a two-package system. Recent environmental toxological studies however indicate that it is very desirable to eliminate free NCO groups from uncured polymers coatings. This would prevent exposure of this toxic
20 material to humans during manufacture, application and in the final product, and the product would be very stable because no NCO groups would be available to react with moisture, etc. To date no satisfactory solution to this problem is available.

25 There is thus a strongly felt need for NCO-free resins and coatings possessing the outstanding performance of urethane materials. Notably there is a strongly felt need for NCO-free resins and coatings possessing the following advantages: high gloss, high impact resistance, good
30 hardness and flexibility, good solvent and chemical resistance, good UV resistance in weathering, and good room temperature cure.

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Disclosure of the Invention

Accordingly, one object of this invention is to provide novel NCO-free resins and cured products thereof possessing the outstanding performance characteristics of urethane materials.

It is another object of this invention to provide novel NCO-free resins and cured products thereof possessing high gloss characteristics.

It is another object of this invention to provide novel NCO-free resins and cured products thereof possessing high impact resistance.

It is another object of this invention to provide novel NCO-free resins and cured products thereof possessing good hardness and flexibility characteristics.

It is another object of this invention to provide novel NCO-free resins and cured products thereof possessing good solvent and chemical resistance.

It is another object of this invention to provide novel NCO-free resins and cured products thereof possessing good UV resistance and weathering characteristics.

It is another object of this invention to provide novel NCO-free resins which cure rapidly at room temperature.

It is another object of this invention to provide a two component kit for preparing NCO-free resins and cured products thereof which have a long life.

The inventor has now discovered NCO-free resins and coatings which satisfy all of the above objects of this invention, and other objects which will become apparent from

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the description of the invention given hereinbelow.

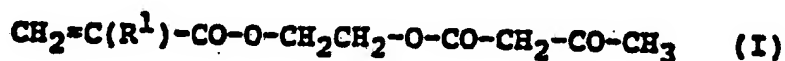
These NCO-free resins and coatings are obtained by curing a two-component mixture. The first component of the mixture is at least one polymer carrying acetoacetyl groups. The second component of this mixture is at least one NCO-free urethane bearing at least two unsaturated end groups (i.e. vinylic end groups). This mixture is cured in the presence of a catalyst having a pKa of 12 to 14.

Best Mode for Carrying Out the Invention

10 The present invention uses two different polymers possessing acetoacetyl groups: an acetoacetylated (meth)acrylic resin and an acetoacetylated polyester. These two different polymers possessing acetoacetyl groups can be either used individually or together in preparing the cured
15 products provided by this invention which includes coatings, articles, adhesives, etc. (vide infra).

Acetoacetylated-(meth)acrylic resin:

In one embodiment, the acetoacetylated acrylic resin is obtained by copolymerizing a mixture containing 10 to 60
20 wt.%, preferably 15 to 35 wt.%, of at least one monomer of formula (I):



and 40 to 90 wt.%, preferably 65 to 85 wt.%, of at least one alkyl (meth)acrylate of formula (II):



25 wherein R is a C₁₋₁₂ linear or branched saturated alkyl group and R¹ is a hydrogen atom or a methyl group.

In another embodiment, the acetoacetylated (meth)acrylic

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resin is obtained by copolymerizing a mixture containing the same ratios as above of at least one monomer of formula (I) together with at least one alkyl (meth)acrylate of formula (II), and in addition 10 to 50 wt.% of styrene.

- 5 These acetoacetylated (meth)acrylic resins have a molecular weight, \bar{M}_n , of from 10,000 to 16,000, preferably 13,000 to 15,000. (\bar{M}_n = number average molecular weight.)

10 The acetoacetylated (meth)acrylic resins may be prepared by polymerization of the monomers by conventional methods using conventional polymerization catalysts. The polymerization is preferably carried out using free-radical-forming catalysts in solution or in emulsion. Conventional emulsifiers and/or protective colloids may be used when the copolymers are prepared in aqueous emulsion.

- 15 When the polymer is prepared in solution, in addition to water, suitable organic solvents which can be used include aromatic hydrocarbons such as benzene, toluene and xylene, ketones such as methylethylketone, esters of saturated carboxylic acids such as ethylacetate, butylacetate and methylglycolacetate, alcohols such as
20 methanol, ethanol, isopropanol, nbutanol, isobutanol and glycols and also glycol ethers, for example the methylether of ethylene glycol.

Acetoacetylated polyester resin:

- 25 The polyester functionalized with acetoacetyl groups can be obtained in one of two ways.

30 In one embodiment, the polyester and a C₁₋₄ acetoacetate, e.g. methyl acetoacetate, are subjected to a transesterification reaction. The polyester used has a molecular weight, \bar{M}_n , of 1,000 to 10,000, preferably 1,200 to 8,000, and possesses hydroxyl groups. The hydroxy group-containing polyesters may contain, as the acid derived

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moiety, moieties derived from benzoic acid, p-t-butyl benzoic acid, capric acid, caproic acid, dimethylol propionic acid, α-ethyl butyric acid, 2-ethyl hexanoic acid, adipic acid, azelaic acid, dimethyl glutarate, fumaric acid, 5 isophthalic acid, maleic anhydride, terephthalic acid, citric acid, trimellitic anhydride, pyromellitic dianhydride, and combinations of two or more of these.

The hydroxy compound derived moiety may be derived from amyl alcohol, benzyl alcohol, butyl alcohol, cetyl alcohol 10 (hexadecanol), ethyl alcohol, α-ethyl hexyl alcohol, hexyl alcohol, isobutyl alcohol, isopropyl alcohol, methyl alcohol, octyl alcohol, pentyl alcohol, propyl alcohol, 1,3-butane diol, 1,4-butane diol, 1,2-, 1,3- or 1,4-cyclohexanedimethanol, diethylene glycol, dimethylol 15 propionic acid, dipropylene glycol, ethylene glycol, Ester Diol 204, 1,6-hexanediol, hexylene glycol, neopentyl glycol, 1,5-pentanediol, propylene glycol, tetraethylene glycol, triethylene glycol, trimethylene glycol, trimethylpentanediol, glycerine, trimethylol ethane, 20 trimethylol propane, tris(hydroxyethyl)isocyanurate, pentaerythritol, and combinations of of two or more of these.

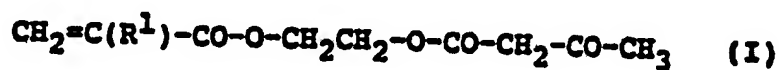
The polyesters have a hydroxyl group content of from 150 to 900 equivalent weight (solids), preferably 150 to 750 25 equivalent weight, -OH (solids).

The transesterification reaction is carried out using conventional methods using conventional transesterification catalysts. The polyester is reacted with the C₁₋₄ alkyl acetoacetate in the presence of a transesterification 30 catalyst to give the acetoacetoxy-resin and a low molecular weight C₁₋₄ alkyl alcohol which is distilled off. Any well known transesterification catalyst may be used, e.g. an acid catalyst like trichloroacetic acid. At least 75% and up to 100%, of the polyester hydroxyl group are esterified.

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In another embodiment, the polyester functionalized with acetoacetyl groups is obtained by subjecting to standard free radical graft polymerization reaction conditions an unsaturated polyester with a monomer of formula (I):



to obtain a product in which at least 70% and up to 100% of the ethylenically unsaturated groups in the unsaturated polyester have been reacted.

10 The unsaturated polyester starting material used has a molecular weight, \bar{M}_n , of from 1,500 to 8,000 preferably 1,500 to 3,500. The diacid component of the unsaturated polyester includes, for example, moieties derived from fumaric acid, maleic acid, itaconic acid, citraconic acid, 15 mesaconic, aconitric acid, and mixtures of two or more of these diacids. Unsaturated polyesters containing fumaric and/or maleic acid-derive moieties are preferred.

The diol component of the unsaturated polyester includes, for example, moieties derived from ethylene 20 glycol, propylene glycol, diethylene glycol (HOCH₂CH₂OCH₂CH₂OH), triethylene glycol (HO(C₂H₄O)₂CH₂OH), polyethylene glycol, dipropylene glycol (mixed isomers), polypropylene glycol, 1,3-butane diol, 1,4-butane diol, 1,6-hexanediol, neopentyl glycol, 1,2-, 1,3- or 1,4- 25 cyclohexanedimethanol, 2,2,4-trimethyl pentane diol, bisphenol A, trimethylolethane, trimethylolpropane, dicyclopentadiene glycol, dimethylol propionic acid, Ester Diol 204, hexylene glycol, 1,5-pentane diol, tetraethylene glycol, monoools of allyl ethers, and mixtures of at least 30 two of the diols. The unsaturated polyester may optionally contain from 10 to 50 wt.% of styrene-derived units.

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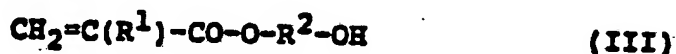
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NCO-free urethane functionalized with unsaturated end groups:

The NCO-free urethane polymer may be a urethane polymer having at least two (meth)acrylate end groups. This polymer 5 can be obtained using one of two different procedures.

In the first procedure, a C₂₋₁₂ linear, branched or cyclic alkyl or arylpolyol having an average of from 2 to 4 hydroxyl groups per molecule is reacted together with a C₂₋₁₂ linear, branched or cyclic saturated alkyl or aryl 10 diisocyanate, triisocyanate or tetraisocyanate, or a mixture of these, at a temperature of from 5 to 20°C using any known conventional catalyst. The reactants are then heated to a temperature of from 40 to 150°C and held at this temperature for a period of time sufficient to reduce the NCO content of 15 the reaction mixture to 4 to 20 wt. %.

A hydroxy substituted alkyl (meth)acrylate of formula (III):



wherein R¹ is a hydrogen atom or a methyl group, and R² is a 20 C₂₋₃ linear or branched saturated alkylene is then added to the reaction mixture. Together with the hydroxy-substituted alkyl (meth)acrylate of formula (III) other vinyl group-containing monomers and polymers may be added optionally with suitable stabilizers. These vinyl containing monomers 25 can be any monomer processing an α,β-unsaturated esters functionality. The stabilizer may, for example, the monomethyl ether hydroquinoline (METHQ) which may be used in an amount of 100 to 500 ppm, preferably 150 to 250 ppm.

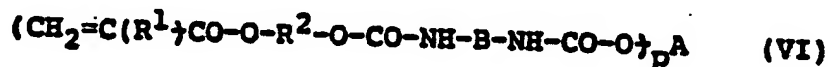
The reaction temperature is maintained at 40 to 150°C 30 until the NCO content of the reaction mixture approaches 0 wt. %, i.e. until the NCO content is not more than 4 wt. %, preferably not more than 2 wt. %, and most preferably not

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more than 1 wt.%. At this time an aliquot of a C₁₋₄ alkyl alcohol, such as methanol, ethanol, etc. is added while maintaining the reaction temperature at from 40 to 150°C until no detectable NCO is obtained. The C₁₋₄ alkyl alcohol is added in an amount corresponding to a OH to NCO ratio of at least 1.5, preferably 1.5 to 3.0, most preferably 1.5 to 2.0. The temperature is maintained at 40 to 150°C until the NCO content reaches a 0.0% NCO is determined by the standard ASTM D 2572-70 (di-butylamine).

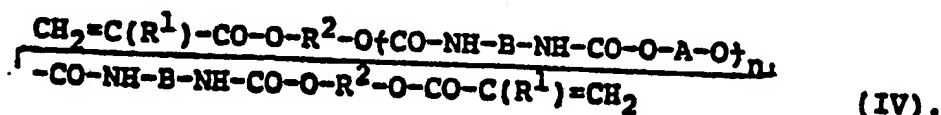
10 Thus in this embodiment, among others, a NCO-free urethane functionalized with unsaturated end groups and of formula (VI) is obtained:



In formula (VI), p is an integer of from 2 to 4. Each R¹ is independently a hydrogen atom or a methyl group. Each R² is independently a C₂₋₃ linear or branched saturated alkylene. Each B is independent a C₂₋₁₂ linear or branched saturated alkylene, or a C₄₋₁₂ cyclic saturated alkylene, or a C₆₋₁₂ arylene. And A is a C₂₋₁₂ linear or branched saturated alkylene group or a C₄₋₁₂ cyclic saturated alkylene group.

The material of formula (VI) is obtained when a diisocyanate is used. However it will be recognized that products having different structures are obtained when 25 triisocyanates and/or tetraisocyanates are used.

In another embodiment, using the process outlined above, a diol is sequentially reacted with a diisocyanate, then with a hydroxy-substituted alkyl (meth)acrylate of formula (III) and then with the C₁₋₄ alkyl alcohol to obtain 30 a product of formula (IV):

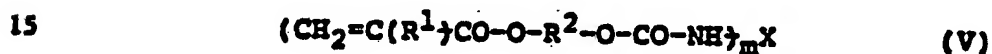


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In formula (VI) each R^1 is independently hydrogen or methyl. Each R^2 is independently a C_{2-3} linear or branched saturated alkylene. Each B is independently a C_{2-12} linear or branched saturated alkylene, or a C_{4-12} cyclic saturated
 5 alkylene, or a C_{6-12} arylene. Each A is independently a C_{2-12} linear or branched saturated alkylene, or a C_{4-12} cyclic saturated alkylene. And n is 1 to 4 for coatings and 1 to 10 for elastomers.

In another embodiment, the NCO-free urethane
 10 functionalized with unsaturated terminal groups is obtained by reacting a diisocyanate and/or a triisocyanate and/or a tetraisocyanate with a hydroxy-substituted alkyl (meth)acrylate of formula (III) to obtain a product of the formula (V):



wherein variables R^1 and R^2 are as defined above, X is the diisocyanate, triisocyanate or tetraisocyanate nucleus or a mixture thereof, and m is 2, 3 or 4.

To obtain the compound of formula (V) the diisocyanate
 20 and/or triisocyanate and/or tetraisocyanate is reacted with the hydroxy substituted alkyl (meth)acrylate formula (III) at a temperature of from 40 to 150°C for a length of time necessary to reduce the NCO content of the reaction mixture to 4 to 20 wt.%. The hydroxy substituted alkyl
 25 (meth)acrylate may be used together with other α,β -unsaturated esters and with vinyl containing monomers and polymers and with suitable stabilizers.

The reaction temperature is maintained until the NCO content approaches 0 wt.%, i.e. is less than 4 wt.%,
 30 preferably less than 2 wt.% and most preferably less than 1 wt.%, at which time an aliquot of a C_{1-4} alcohol similar to that described above is added while maintaining the reaction

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temperature until no detectable NCO is obtained (i.e. until the NCO content is 0.0% as defined by ASTM D 2572-70 (di-butylamine). As discussed supra, the Cl-4 allyl alcohol is added in an amount corresponding to a NCO to OH ratio of at least 1.5, preferably 1.5 to 20. The product thus obtained has a molecular weight \bar{M}_n , of 200 to 8,000 preferably 400 to 4,000.

When the NCO-free urethane, functionalized with unsaturated end groups is prepared (e.g. from a diol to obtain the material of formula (IV) or from a polyol to obtain the material of formula (VI)), it will be appreciated that a molar excess of the isocyanate (viz. the diisocyanate, triisocyanate and/or tetraisocyanate) over the hydroxy compound must be used in the preparation of the prepolymer. In this reaction formation of the isocyanate-prepolymer may be assisted by the use of catalysts known in the art to assist polyurethane formation. For example, these include tertiary amines, and methyl salts, e.g. stannous octoate and particular dibutyl tin dilaurate.

The reaction of the hydroxy compound and the Isocyanate may produce a viscous urethane prepolymer and, especially when the degree of polymerization is large, the prepolymer may be solid. It is desirable in these circumstances that the reaction of the hydroxy compound and the isocyanate be effected in the presence of an inert diluent. Similarly, where the urethane prepolymer is very viscous or solid, further reaction of the prepolymer is desirably effected in the presence of an inert diluent.

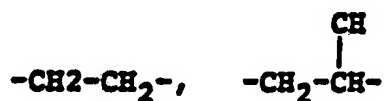
The diluent should be substantially free of groups which are reacted with isocyanate groups, at least to such an extent that the diluent does not interfere with the formation of the prepolymer. In the preparation of the material of formula (VI), the diluent can of course be the hydroxy substituted (meth)acrylate of formula (III).

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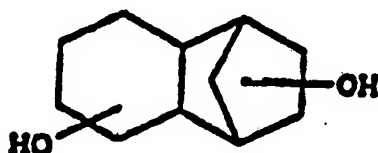
When the urethane prepolymer is prepared in an inert diluent, the prepolymer may be separated from the diluent, e.g. by evaporation of the diluent or by the addition to the diluent of a non-solvent or the prepolymer.

- 5 The C₂₋₁₂ linear, branched or cyclic alkyl or aryl polyol which can be used in the present invention include methylene glycol, propylene glycol, butylene glycol, glycerine, trimethylolethane (TME), trimethylolpropane (TMP) and pentaerythritol, or combinations of these materials.
- 10 Examples of diols and polyols which do not have cyclic groups in the chain include, for example, ethylene glycol and propylene glycol, in which case A has the structure



- Butylene glycol, diethylene glycol 1,3-butane diol, 1,4-
 15 butane diol, dipropylene glycol, 1,6-hexanediol, hexylene glycol, neopentyl glycol, 1,5-pentanediol, tetraethylene glycol, triethylene glycol, trimethylene glycol, trimethyl pentane diol, trimethylol ethane, or trimethylol propane, and derivatives of these materials in which one or more of
 20 the carbon atoms are substituted by atoms or groups which are unreactive towards hydroxyl and isocyanate group may be used.

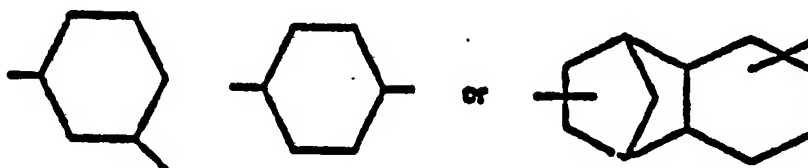
- Examples, of diols containing cyclic groups which may be used in the preparation of the urethane prepolymer
 25 include, for example, cycloalkane diols, e.g. 1,2-, 1,3- or 1,4-cyclohexane diol and a diol having the structure



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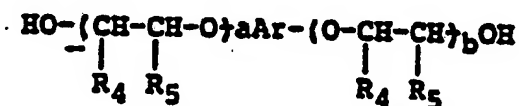
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in which case the group A in the urethane prepolymer has the structure



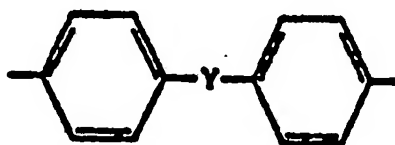
respectively. Other suitable diols include, for example, cycloalkane dialkanols, e.g. 1,2-, 1,3- or 1,4-cyclohexane dimethanol or 1,2-, 1,3- or 1,4-cyclohexane diethanol; polycycloalkane diols, polycycloalkane dialkanols, aryl dialkanols and condensates of alkylene oxides with aromatic compounds containing two phenolic groups.

10 Other diols which can be used are diols of the structure



that is, oxyalkylated derivatives of phenolic compounds, where R₄ and R₅ are hydrogen atoms or C₁₋₄ alkyl groups, e.g. methyl, and Ar is a divalent aromatic group in which each free valency is on an aromatic carbon atoms. and in which a+b together preferably total not more than 8 and a is preferably not greater than b+3.

Ar may be mononuclear, e.g. as in phenylene, fused polynuclear as in naphthalene or anthracene, or preferably has the structure

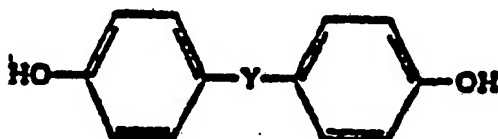


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in which Y is a divalent link, e.g. -O-, -SO₂-, -CO- or -CH₂- or a substituted derivative of -CH₂- e.g.



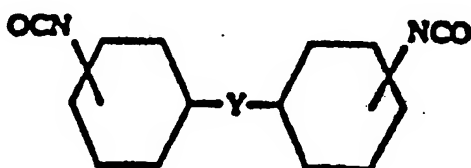
Suitably, one of the groups R₄ and R₅ is hydrogen and the other is methyl, or both R₄ and R₅ are hydrogen. That is, the diol may be prepared by reaction of propylene oxide or ethylene oxide with a phenolic compound having the structure HO-Ar-OH, preferably



10 Preferably a+b is not greater than 4.

Diisocyanates containing cyclic groups which may be used to prepare the urethane prepolymer include, for example, diisocyanates in which the chain between the free valencies is provided with at least one aromatic group or at least one cycloaliphatic group, or in which the chain between the free valencies includes in combination at least one aromatic and at least one cycloaliphatic group.

Cycloaliphatic diisocyanates include for example, diisocyanates of the structure:



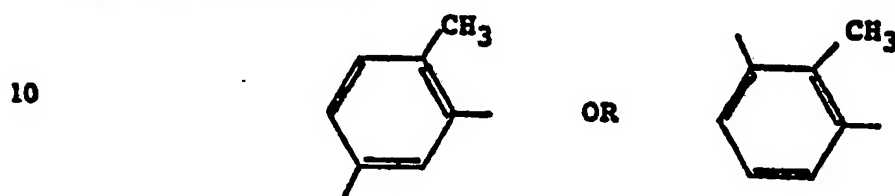
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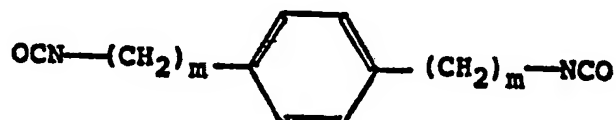
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where -Y- is a divalent link which may be, for example, -CH₂- or substituted derivative thereof, -O-, -SO₂-, -CO-, and the isocyanate groups are linked meta- or para- to the groups Y. A particular example is 4,4'-5 dicyclohexylmethane diisocyanate.

Aromatic diisocyanates which may be used include, for examples, 2,4- or 2,6-tolylene diisocyanate, or mixtures thereof, in which case the divalent group B or X has the structure

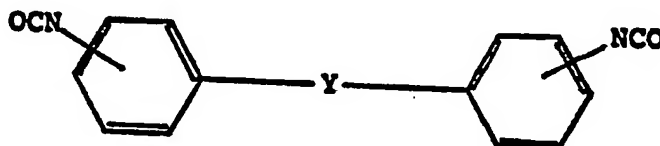


or a combination of said structures. Another suitable aromatic diisocyanate is that having the structure



where m is a whole number chosen such that there are preferably not more than 20 atoms between cyclic groups in the urethane prepolymer derived therefrom. A suitable diisocyanate having the latter structure is xylylene diisocyanate.

Another suitable diisocyanate is that having the structure:



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where Y is a divalent link which may have the designations hereinbefore described and in which the isocyanate groups are linked meta or para to the group Y. A preferred example is 4,4'-diisocyanatodiphenyl methane.

5 Diisocyanates which do not contain cyclic groups may be used in the production of the urethane prepolymer. Suitable such diisocyanates include, for example, tetramethylene diisocyanate, pentamethylene diisocyanate and hexamethylene diisocyanate, in which case the divalent group B or X will
10 have the structure $-(CH_2)_4-$, $-(CH_2)_5-$ or $-(CH_2)_6-$.

Preferred isocyanates are 1,6-hexamethylenediisocyanate (HDI), trimethylhexamethylenediisocyanate (TMDI), isophoronediiisocyanate (IPDI), toluene diisocyanate (TDI) and 4,4'-diphenyl methane diisocyanate (MDI), and
15 combinations of these.

A polyisocyanate-containing material may be obtained by reacting a polyol of the formula



with a diisocyanate of the formula



where the diisocyanate is used in a molar amount of $2(x)$ relative to the polyol. The reaction product obtained has the structure



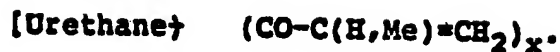
25 and is reacted with a hydroxy-substituted alkyl (meth)acrylate of the formula



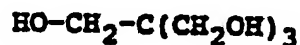
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which is used in a molar amount of 2(x) to provide a product of the formula



In the above description, R is C₅₋₁₀₀ linear or branched or cyclic alkyl, x is an integer of from 4 to 10, R' is C₆₋₁₅ linear or branched or cyclic alkyl, and R'' is C₂₋₆ linear or branched or cyclic alkyl. Examples of R(OH)_x include, when R = C₅ and x = 4, pentaerythritol, a material of the formula



- 10 Also when R is C₆₋₁₀₀ alkyl, x may be > 4, e.g. the hydroxy-substituted polyester may be used for R(OH)_x.

Uses:

The materials obtained by curing the two components used in the present invention may be used in any application in which polyurethanes are used. These applications include acoustic foams, building products, contact lenses, craniofacial reconstruction, cushioning, fibers, films, foam insulation, insulation, mouth protectors, packings, recreational surfaces, coatings, fabric coatings, concrete waterproofing, leather coatings, magnetic tape binders, elastomeric blends, sealing applications, etc.

A salient advantage of the compositions of the present invention is their curing characteristics. The compositions readily cure at temperatures below 120°C, preferably below 100°C, and they can also be cured easily at room temperature.

One of the uses of the present compositions is in coating varied articles which may be coated with polyurethane coatings. These articles include e.g.,

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automobiles (e.g. exterior of automobiles, etc.), fabrics (e.g. raincoats, clothing, shoes, umbrellas), etc. These articles may be obtained by using known procedures used with polyurethanes. The present compositions can also be used as
5 sealants (e.g. for double pane windows).

Coatings and articles in accordance with the present invention are obtained by curing at least one of the polymers functionalized with acetoacetyl groups together with at least one NCO-free urethane functionalized with
10 unsaturated end groups in the presence of a catalyst. The catalysts used must have a pKa of from 12 to 14. Suitable catalysts which may be used include 1,8-diazo-[5.4.0]-bicycloundecene, tetramethyl guanidine, 1,4-dihydropyridines, and 2-allyl-N-alkyl imidazoline.

15 The acetoacetylated acrylic resin and/or acetoacetylated polyester resin component, on the one hand, and the NCO-free resin component, on the other hand, are reacted in an amount of 1 to 0.8 to 1.2, respectively, preferably 1 to ca. 1, these amounts being measured in
20 equivalents of acetoacetyl groups to equivalents of vinylic groups in the NCO-free resin. The catalyst is used in an amount of 0.2 to 3.0 wt.%, preferably 0.2 to 1.0 wt.%. These amounts are based on the amount of resin solid.

The two-component coating systems of the present
25 invention are isocyanate-free. They are easy to apply using known techniques, requiring the use of only conventional existing equipment without the need for taking special safety precautions. The coatings and articles obtained from these compositions possess the outstanding performance
30 characteristics of polyurethanes.

Other features of the invention will become apparent in the course of the following descriptions of exemplary embodiments which are given for illustration of the invention and are not intended to be limiting thereof.

SUBSTITUTE SHEET

The list below identifies the abbreviations used in the experimental section.

	<u>MATERIALS</u>	<u>SOURCE</u>
5	1. Acetoacetoxyethyl Methacrylate Monomer (AAEM) CAS No. 21282-97-3	EASTMAN CHEMICAL
	2. Butyl Acrylate Monomer (BA) CAS No. 141-32-2	ROHM & HAAS
	3. Butyl Methacrylate Monomer (BMA) CAS No. 97-88-1	ROHM & HAAS
10	4. n-Butyl Acetate CAS No. 123-86-4	UNION CARBIDE
	5. BYK 300 (Paint Additive)	BYK MALLINCKRODT CHEMISCHE PRODUKTE
15	6. BYK 306 (Paint Additive)	BYK MALLINCKRODT CHEMISCHE PRODUKTE
	7. Desmodur H 1,6-Hexamethylene Diisocyanate (HDI) CAS No. 822-06-0	MOBAY CHEMICAL CORP.
20	8. Desmodur W Methylene Bis(4-cyclohexylisocyanate) CAS No.	MOBAY CHEMICAL CORP.
	9. 1,8-Diaza-bicyclo[5,4,0]undecene-7 (Amicure DBU / DBU) CAS No. 6674-22-2	AIR PRODUCTS
25	10. Ektapro EEP Solvent (EEP) CAS No.	EASTMAN CHEMICAL
	11. 1,6-Hexanediol Diacrylate (HDODA) CAS No. 13048-33-4	INTEREZ
30	12. High Flass Naphtha (Unical 86) CAS No.	WARUM CHEMICAL
	13. Hydroxyethyl Acrylate Monomer (ROCYL 420 / HEA) CAS No. 818-61-1	ROHM & HAAS
35	14. Hydroxypropyl Acrylate Monomer (ROCYL 430 / HPA) CAS No. 25584-83-2	ROHM & HAAS

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- | | | | | |
|----|-----|--|--------------------|---------------|
| | 15. | Isophorone Diisocyanate
(IPDI) | CAS No. 4098-71-9 | HUELS |
| 5 | 16. | IPDI-T 1890 L
(Isocyanurate of IPDI) | CAS No. | HUELS |
| | 17. | Isocyanate 81
(Modified 4,4'-Diphenylmethane
Diisocyanate) | CAS No. | BASF |
| 10 | 18. | 4,4'-Diphenyl Methane Diisocyanate
(MONDUR M, MDI) | CAS No. | MOBAY |
| | 19. | Mercapto Ethanol | CAS No. 60-24-2 | ALDRICH/BASF |
| 15 | 20. | Methyl Methacrylate Monomer
(MMA) | CAS No. 80-62-6 | ROHM & HAAS |
| | 21. | MPA-2000
(Anti-setting agent) | CAS No. | NL CHEMICALS |
| 20 | 22. | Styrene Monomer | CAS No. 100-42-5 | POLYSAR |
| | 23. | TIOXIDE RCR 60;
(Titanium Dioxide, Pigment) | CAS No. 13463-67-7 | TIOXIDE CORP. |
| 25 | 24. | Toluene Diisocyanate
(MONDUR TD-80 TDI) | CAS No. | MOBAY |
| | 25. | Trimethylolpropane Ethoxy Triacrylate
(TMPEOTA) | CAS No. 28961-43-5 | SARTOMER |
| 30 | 26. | Trimethylolpropane Triacrylate
(TMPTA) | CAS No. 15625-89-5 | INTEREZ |
| | 27. | Trimethylol Ethane
(TME) | CAS No. 77-85-0 | IMC |
| 35 | 28. | Trimethylol Propane
(TMP) | CAS No. 77-99-6 | CELANESE |
| | 29. | Trimethylhexamethylene Diisocyanate
(TMDI) | CAS No. 16938-22-0 | HUELS |
| 40 | 30. | VAZO 67
2,2'-Azobis(2-Methylbutyronitrile) | CAS No. 13472-08-7 | DU PONT |

SUBSTITUTE SHEET

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|----|-----|--|-------------------|---------------------------|
| | 31. | VAZO 64
Azobisisobutyronitrile | CAS No. 78-67-1 | DU PONT |
| | 32. | Xylol | CAS No. 1330-20-7 | HARRISONS &
CROSSFIELD |
| 5 | 33. | Propylene Glycol Monomethyl Ether Acetate
(EKTASOLVE PM Acetate, PMA) | CAS No. | EASTMAN CHEMICAL |
| | 34. | Monomethyl Ether of Hydroquinone
(MEHQ) | CAS No. 150-76-5 | EASTMAN CHEMICAL |
| 10 | 35. | Dibutyltin Dilaurate
(T-12, DBTL) | CAS No. 77-58-7 | M & T CHEMICAL |
| | 36. | Methyl Ethyl Ketone
(MEK) | CAS No. 78-93-3 | HARRISON &
CROSSFIELD |

SUBSTITUTE SHEET

FORMULATIONS OF TWO COMPONENT NCO-FREE WHITE PAINT**RAW MATERIALS OF PART ONE:**

1. White Paint - A -- Resin A, GX-75-146
2. White Paint - B -- Resin B, GX-75-162

5 RAW MATERIALS OF PART TWO:

2. ETMPTA -- Ethoxylated trimethylolpropane triacrylate
4. NCO-free acrylic urethane-B (NFAU-B) -- GX-81-170
5. NCO-free acrylic urethane-C (NFAU-C) -- GX-87-3
6. NCO-free acrylic urethane-D (NFAU-D) -- GX-87-37
- 10 7. NCO-free acrylic urethane D (NFAU-D) -- GX-87-37

CATALYST:

DBU -- 1,8-diaza-[5,4,0]-bicycloundecene.

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NCO-FREE WHITE ACRYLIC ENAMEL FORMULATION**PART ONE:** White Paint-X

Where, X = White Paint-A, White Paint-B or
White Paint-A, and White Paint-B.

5 PART TWO: Crosslinking Agent-Y

Where, Y = TMPTA, ETMPTA or TMPTA and ETMPTA

EQ. WT. Ratio of Part One/Part Two = 1/0.8-1

CATALYST: DBU, 0.4-1.0% TRS

SUBSTITUTE SHEET

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NCO-FREE WHITE ACRYLIC-URETHANE ENAMEL FORMULATION**PART ONE: White Paint-X**

Where, X = White Paint-A, White Paint-B or
White Paint-A, and White Paint-B.

5 PART TWO: Crosslinking Agent-Y

Where, Y = NFAU-A, NFAU-B, NFAU-C, NFAU-D, NFAU-E
or mixture of both e.g., NFAU-A/NFAU-
B, ETMPTA/NFAU-D, NFAU-D/NFAU-E etc.

EQ. WT. Ratio of Part One/Part Two = 1/0.8-1.0

10 **CATALYST:** DBU, 0.4-1.0% TRS

SUBSTITUTE SHEET

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Preparation of hydroxy-group containing polyester:
GX-60-178 (GX-59-67):

RAW MATERIALS

	A. Neopentyl Glycol (EASTMAN)	944.4	GMS
5	B. Pentaerythritol (CELANESE).....	126.6	GMS
	C. Isophthalic Acid (AMOCO).....	874.9	GMS
	D. Adipic Acid (BASF).....	493.9	GMS
	E. Benzoic Acid (BAYER).....	143.8	GMS
		<u>2583.5</u>	<u>GMS</u>

10 PROCEDURE

1. Charge neopentyl glycol and adipic acid into a 5-L flask equipped with agitator, sample tube, thermometer, nitrogen purge, packed partial condenser, water trap and total condenser.
- 15 2. Increase temperature to 130+5C. at 130C weigh in isophthalic acid, pentaerythritol and benzoic acid.
3. Heat to 215+5C (max.) and maintaining an exit vapor temperature at 100+5C (max.) on partial condenser until the distillate exit temperature falls below 90C. Allow reaction mixture to cool to 150C.
- 20 4. Remove the packed partial condenser and start addition of xylol to establish solvent reflux processing and hold at 215+5C until an acid value of 10 is reached.
5. Cool to 150C and dilute to 80 NVM% with n-butyl acetate.

25 SPECIFICATIONS:

	Solids content %.....	80
	Viscosity.....	88", 24-5
	AN.....	10
	Color.....	1
30	WPG (IMP.).....	11.0
	Solvent.....	n-butyl acetate
	-OH, Eq.Wt. (solids).....	708

SUBSTITUTE SHEET

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Preparation of hydroxy-group containing polyester:
GX-60-163 (GX-59-80):

RAW MATERIALS

	A. Adipic Acid (BASF).....	1523.5	GMS
5	B. Trimethylol Propane (CELANESE).....	561.0	GMS
	C. Propylene Glycol (DOW).....	816.0	GMS
		<u>2900.5</u>	<u>GMS</u>

PROCEDURE

1. Charge adipic acid, trimethylol propane, and propylene glycol into a 5-L flask equipped with agitator, sample tube, thermometer, nitrogen sparge, packed partial condenser, water trap and total condenser.
2. Heat to 215+5C (max.) and maintaining an exit vapor temperature at 100+5C (max.) on partial condenser until the distillate exit temperature falls below 90C. Allow reaction mixture to cool to 150C.
3. Remove the packed partial condenser and start addition of xylol to establish solvent reflux processing and hold at 215+5C until an acid value of < 5 is reached.

SPECIFICATIONS: ;

20	Solids content %	96
	Viscosity.....	88", 24-5 25
	AN.....	1.5
	Color.....	1
	WPG (IMP.).....	11.4
25	Solvent.....	xylol
	-OH,Eq.Wt.(solids)	192

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Preparation of hydroxy-group containing polyester:
GX-60-156 (GX-59-79):

RAW MATERIALS

	A. Adipic Acid (BASF).....	1385.0	GMS
5	B. Trimethylol Propane (CELANESE).....	510.0	GMS
	C. Ethylene Glycol (STANCHEM).....	605.0	GMS
		<hr/>	
		2500.0	GMS

PROCEDURE

- 10 1. Charge adipic acid, trimethylol propane, and ethylene glycol into a 5-L flask equipped with agitator, sample tube, thermometer, nitrogen sparge, packed partial condenser, water trap and total condenser.
- 15 3. Heat to 215+5C (max.) and maintaining an exit vapor temperature at 100+5C (max.) on partial condenser until the distillate exit temperature falls below 90C. Allow reaction mixture to cool to 150C.
4. Remove the packed partial condenser and start addition of xylol to establish solvent reflux processing and hold at 215+5C until an acid value of < 5 is reached.
- 20 5. Cool to 150C; and dilute to 80 NVM% with n-butyl acetate.

SPECIFICATIONS:

	Solids content %	97
	Viscosity.....	52", 23-4
	AN.....	0.5
25	Color.....	1
	WPG (IMP.).....	11.8
	Solvent.....	xylol
	-OH, Eq.Wt.(solids)	181

SUBSTITUTE SHEET

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NCO-FREE ACRYLIC WHITE PAINT A
PART 1
GRIND PASTE
GX-82-10(GX-75-106)

5 PREMIX

	GP-GX-75-146 (NCO-free acrylic)	268.5 GMS
	Xylol	80.5 GMS
	EEP	40.0 GMS
10	MPA-2000X	3.6 GMS
	BYK 300	2.9 GMS

DISPERSE AT HIGH SPEED IN A COWELS STIRRER FOR 15 MINUTES

SIFT IN

	Tioxide RCR 60	220.0 GMS
--	----------------------	-----------

15 DISPERSE AT HIGH SPEED AGAIN FOR 30 MINUTES AND THEN
SANDMILL TO 7H

MILL CLEANUP

	GP-GX-75-146	68.3 GMS
	Xylol	20.0 GMS

PREMIX FOR MILL FLUSH

20	Xylol	60.0 GMS
	EEP	30.0 GMS

LETDOWN MIXTURE

	GP-GX-75-146	214.7 GMS
	n-Butyl acetate	40.0 GMS

25 PREMIX FOR LETDOWN

SPECIFICATIONS:

	Viscosity (Stormer).....	62 KU
	Dispersion (Hegmen).....	7 H
	Hiding (CRIPTOMETER).....	894
30	SAG (thousand of an inch).....	4 - 5
	Solids content %, by wt.	48.0

SUBSTITUTE SHEET

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NCO-FREE ACRYLIC RESIN
(GX-75-146)

RAW MATERIALS

5	A.	Methyl methacrylate	263.7	GMS
		Butyl methacrylate	300.0	GMS
		Acetoacetoxyethyl methacrylate	196.3	GMS
	B.	VAZO 64	8.0	GMS
		PMA/Xylol (20/80)	255.0	GMS
10	C.	Xylol	503.0	GMS
	D.	Mercapto ethanol	0.3	CC

PROCEDURE

1. Charge RM-C into 3 L flask. Place RM-A and RM-B in respective addition funnels.
- 15 2. Heat xylol to 105+5 C and then start addition of RM-A and RM-B at a rate indicated on data and results. Maintain temperature at 105+5 C.
3. Once RM-A and RM-B are completely added, wait for one hour then take the first sample and add 0.3 g of VAZO 64 into reaction flask.
- 20 4. For every 30 minutes, take sample add add 0.3 g of VAZO 64.
5. If the solids content of sample reached 49.5% of NVM, add another 0.3 g of VAZO 64 and wait for 30 minutes. Then turn off heat, add 0.3 CC of RM-D.

25 CHARACTERISTICS

30	NVM %.....	50+1
	A.N.....	20+1
	Viscosity.....	U
	Color.....	1
	WPG.....	9.90+0.05
	Solvent.....	Xylol
	Mn.....	15145
	Polydisp.....	1.7965

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NCO-FREE ACRYLIC WHITE PAINT A

PART 1

GRIND PASTE
GX-82-11(GX-75-108)5 PREMIX

	GP-GX-75-162 *Acrylic polymer)	250.0 GMS
	Xylol	90.0 GMS
	High flash napht.	30.0 GMS
10	MPA-2000X	3.6 GMS
	BYK 300	3.0 GMS

HSD AT HIGH SPEED FOR 15 MINUTES

SIFT IN

	Tioxide RCR 60	280.0 GMS
--	----------------------	-----------

HSD FOR 30 MINUTES AND THEN SANDMILL TO 7H

15

MILL CLEANUP

	GP-GX-75-162	65.0 GMS
	Xylol	22.0 GMS

PREMIX FOR MILL FLUSH

20	Xylol	60.0 GMS
	High flash napht.	20.0 GMS

PREMIX FOR MILL RINSE

LETDOWN MIXTURE

	GP-GX-75-162	200.5 GMS
	Xylol	30.0 GMS

25 PREMIX FOR LETDOWNSPECIFICATION:

30	Viscosity	63 KU
	Dispersion	7 H
	Hiding	970
	SAG	4 - 5
	Solids content %, BY wt.	56.7

.SUBSTITUTE SHEET

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NCO-FREE ACRYLIC RESIN
(GX-75-162)

RAW MATERIALS

5	A. Butyl acrylate	294.6	GMS
	Styrene	232.8	GMS
	Acetoacetoxyethyl methacrylate	232.4	GMS
B.	VAZO 64	8.0	GMS
	PMA/Xylol (20/80)	255.0	GMS
C.	Xylol	250.0	GMS
10	D. Mercapto ethanol	0.3	CC

PROCEDURE

1. Charge RM-C (xylol) into 3 L flask. Place RM-A (monomers) and RM-B (initiator solution) in respective addition funnels.
- 15 2. Heat xylol to 105+5 C and then start addition of RM-A and RM-B at a rate indicated on data and results. Maintain temperature at 105+5 C.
3. Once RM-A and RM-B are completely added, wait for one hour then take first sample and add 0.3 g of VAZO 67 into reaction flask.
- 20 4. For every 30 minutes, take sample add add 0.3 g of VAZO 67.
- 25 5. If the solids content of sample reached 59.5% NVM, add one more 0.3 g of VAZO 67 and wait for at least 30 minutes, then remove heat, add 0.3 CC of RM-D (mercapto ethanol).

SPECIFICATIONS

30	NVM %	60+1
	A.N.	20+1
	Viscosity	V
	Color	1
	WPG	10.00+0.05
35	Solvent	Xylol
	Mn	13390
	Polydisp	2.5530

SUBSTITUTE SHEET

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NFAU - A

NCO-FREE ACRYLIC URETHANE

GX-87-52

RAW MATERIALS

5	A.	IPDI-T 1890 L	700.00	GMS
	B.	Hydroxypropyl acrylate	247.00	GMS
		MEHQ	0.05	GMS
	C.	DBTL (T-12).....	0.37	GMS
		n-Butyl acetate.....	5.00	GMS
10	D.	n-Butyl acetate.....	105.43	GMS
			<u>1057.85</u>	<u>GMS</u>

PROCEDURE

1. Charge RM-A, RM-D and RM-C into reactor at R.T.
2. Heat to 75+5 C and maintain at 75+5 C when RM-B is added within one hour under dry pressure air.
3. Hold the reactor temperature at 75+5 C until NCO% drop to 1.0 % cool to 60+5 C and 20 ml of MECH is added.
4. Maintain at 60+5 C until NCO% = 0.0

20 SPECIFICATIONS

	NVM %	73.8
	Viscosity (Gardner).....	58", Z3-4
	Color (Gardner).....	1
	NCO%	0.0
25	WPG (IMP.) (SP. GR.).....	10.57
	Solvent	n-butyl acetate
	Eq.Wt.	387.89 (solids)
		525.1 (73.87 %)

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NFAU - B

NCO-FREE ACRYLIC URETHANE

GX-81-170 (GX-75-159)

RAW MATERIALS

5	A.	Trimethylol propane (TMP)	112.50	GMS
		MEK	250.00	GMS
	B.	Isophorone diisocyanate (IPDI)	555.50	GMS
		MEK	58.33	GMS
10	C.	Hydroxyethyl acrylate (HEA)	252.80	GMS
		HQME05	GMS
	D.	T-1294	GMS
		MEK	5.25	GMS
			<u>1235.37</u>	<u>GMS</u>

PROCEDURE

- 15 1. Charge RM-A into reactor at room temperature.
2. Hold at 20-30 C when RM-B is added within 15 minutes.
3. Heat to 80+5 C and maintain at 80+5 C until NCO% reduced to 10.
- 20 4. Continue to hold at 80+5 C with RM-C is added within 15 minutes.
5. Maintain the reaction solution at 80+5 C until NCO% drops to 0.5, cool to 60+5 C and then 15 ml of methanol is added.
6. Hold at 60+5 C until NCO% = 0.

25 SPECIFICATIONS

	NVM %	78
	Viscosity	Z6
	Red. Vis.	10.8", W
		at 70% NVM
30	Color	1
	NCO%	0.0
	WPG	10.63
	Solvent	MEK

-SUBSTITUTE SHEET

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NFAU - C

NCO-FREE ACRYLIC URETHANE

GX-87-3 (GX-75-160)

RAW MATERIALS

5	A. Trimethylol propane (TMP)	130.44	GMS
	MEK	293.00	GMS
	B. Desmodur H	487.54	GMS
	MEK	113.04	GMS
10	C. Hydroxyethyl acrylate (HEA)	314.40	GMS
	HQME06	GMS
	D. T-1249	GMS
	MEK	5.20	GMS
		<u>1344.11</u>	<u>GMS</u>

PROCEDURE

- 15 1. Charge RM-A into reactor at room temperature.
2. Hold at 20-25 C when RM-B is added within 15 minutes.
3. Cool down to 15±5 C when RM-D is added within 5 minutes.
- 20 4. Heat to 50-60 C and maintain at 50-60 C until NCO% reduced to a value of 12.0 [4-20% (9-12 preferred)].
5. Hold at 50-60 C when RM-C is added within 15 minutes.
6. Maintain at 50-60 C until NCO% reduced to 0.5 and then 15 ml of methanol is added.
7. Hold at 50-60 C until NCO% = 0.

25 SPECIFICATIONS

30	NVM %	72.57
	Viscosity	11", V
	Color	1
	NCO%	0.0
	WPG	10.47
	Solvent	MEK

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NFAU - D

GX-87-37 (GX-75-167)

RAW MATERIALS

5	A. Trimethy hexamethylene diisocyanate (TMDI)	210.00	GMS
	B. Hydroxypropyl acrylate (HPA).....	247.00	GMS
	C. DBTL (T-12).....	.25	GMS
	D. MEK.....	.05	GMS
		<u>571.30</u>	<u>GMS</u>

10 PROCEDURE

1. Charge RM-A, RM-D and RM-C into reactor at room temperature.
2. Heat to 65+5 C and hold at 65+5 C when RM-B and RM-E are added.
- 15 3. Maintain the reaction temperature at 65+5 C until NCO% down into 1.0 and 15 ml of methanol is added.
4. Hold at 65+5 C until NCO% = 0.

SPECIFICATIONS

20	Solids Content	78.3
	Viscosity	C
	Color	1
	NCO%	0.0
	WPG (IMP)	10.41
	Solvent.....	MEK

SUBSTITUTE SHEET

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NFAU - E

GX-87-44

RAW MATERIALS

5	A. Trimethylol propane (TMP)	115.30	GMS
	MEK	268.00	GMS
	B. Trimethyl hexamethylene diisocyanate (TMDI)	538.80	GMS
	MEK	50.00	GMS
10	C. Hydroxypropyl acrylate (HPA)	268.06	GMS
	HQME	0.06	GMS
	D. T-12	0.30	GMS
	MEK.....	5.50	GMS
		<u>1246.69</u>	<u>GMS</u>

PROCEDURE

- 15 1. Charge RM-A into reactor at room temperature.
2. Hold at 20-25 C when RM-B is added (30 minutes) under N and then RM-D is added.
3. Heat to 65+5 C and maintain at 65+5 C until NCO% reduced to 10.0%.
- 20 4. Continue to hold at 65+5 C when RM-C is added within one hour.
5. Maintain at 65+5 C until NCO% down to 1.0% and then 15 ml of methanol is added.
6. Hold at 65+5 C until NCO% = 0.

25 SPECIFICATIONS

30	Solids content %	75.0
	Viscosity	12", W-X
	Colour	1
	NCO%	0.0
	WPG (IMP)	10.23

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GP-GX-81-155

NCO-FREE ACRYLIC PAINT

COLOR: RED

GRIND PASTE

PREMIX

5	GP-GX-75-162 Acrylic polymer	125.0	GMS
	Xylol	45.0	GMS
	MPA-2000X	3.6	GMS
	BYK 300	3.0	GMS

HSD AT HIGH SPEED FOR 15 MINUTES

SIFT IN

10	Moly Orange 2565	65.1	GMS
	Host Violet ER02	8.9	GMS
	Bon-Maroon-6002	0.9	GMS

HSD FOR 30 MINUTES AND THEN SANDMILL TO 7H

MILL CLEANUP

15	GP-GX-75-162	105.0	GMS
	Xylol	15.0	GMS

PREMIX FOR MILL FLUSH

Xylol	95.0	GMS
-------------	------	-----

LETDOWN MIXTURE

20	GP-GX-75-162	368.0	GMS
	Xylol	100.00	GMS

PREMIX FOR LETDOWN

SPECIFICATION:

25	Viscosity	58	KU
	Dispersion	7	H
	Hiding	646	
	SAG	6 - 7	
	Solids content %, By V.	41.2	
	Total paint	934.5	GMS

SUBSTITUTE SHEET

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GP-GX-81-137

NCO-FREE ACRYLIC PAINT

COLOR: GREEN

GRIND PASTE

PREMIX

5	GP-GX-75-162	268.5	GMS
	Xylol.....	28.8	GMS
	MPA-2000X.....	3.6	GMS
	BYK 300.....	3.0	GMS

HSD AT HIGH SPEED FOR 15 MINUTES

SIFT IN

10	I.A.F. Compound	1.8	GMS
	Sandor-Green-GLS	2.4	GMS
	LT Yel 09-425 2p	73.3	GMS
	Irgalit-Blue-BCA	1.8	GMS
	Tioxide RCR 60	3.6	GMS
15	Regal 400R Black	0.3	GMS

HSD FOR 30 MINUTES AND THEN SANDMILL TO 7H

MILL CLEANUP

	GP-GX-75-162	74.8	GMS
	Xylol	30.0	GMS
20	PREMIX FOR MILL FLUSH		
	Xylol	82.7	GMS

FOR MILL RINSE

LETDOWN MIXTURE

25	GP-GX-75-162	543.9	GMS
	Xylol	92.1	GMS

PREMIX FOR LETDOWN

SPECIFICATION:

30	Viscosity	60	KU
	Dispersion	7	H
	Hiding	726	
	SAG	6 - 7	
	Solids content %, By V.	43.63	
	Total paint	990.3	GMS

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GP-GX-81-148

NCO-FREE ACRYLIC PAINT

COLOR: YELLOW

GRIND PASTE

PREMIX

5	GP-GX-75-162	236.4	GMS
	Xylol.....	127.2	GMS
	MPA-2000X.....	3.8	GMS
	BYK 300.....	3.1	GMS

HSD AT HIGH SPEED FOR 15 MINUTES

SIFT IN

10	Light Yel 2361	142.2	GMS
	Tioxide RCR 60	52.3	GMS
	Chrome Yel 2165	47.4	GMS
	Ferrite-Yel-305	7.2	GMS

HSD FOR 30 MINUTES AND THEN SANDMILL TO 7H

15 MILL CLEANUP

	GP-GX-75-162	100.0	GMS
	Xylol	39.1	GMS

PREMIX FOR MILL FLUSH

	Xylol	80.9	GMS
--	-------------	------	-----

20 LETDOWN MIXTURE

	GP-GX-75-162	236.4	GMS
	Xylol	42.7	GMS

PREMIX FOR LETDOWN

SPECIFICATION:

25	Viscosity	61	KU
	Dispersion	7	H
	Hiding	894	
	SAG	4 - 5	
	Solids content %, By V.	40.8	
30	Total paint	1118.7	GMS

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FORMULATIONS OF TWO COMPONENT NCO-FREE WHITE PAINT**RAW MATERIALS OF PART ONE:**

1. White Paint - A -- Resin A, GX-75-146
2. White Paint - B -- Resin B, GX-75-162

5 RAW MATERIALS OF PART TWO:

1. TMPTA -- Trimethylolpropane triacrylate.
2. ETMPTA -- Ethoxylated trimethylolpropane triacrylate
3. NCO-free acrylic urethane-A (NFAU-A) -- GX-81-161
4. NCO-free acrylic urethane-B (NFAU-B) -- GX-81-170
- 10 5. NCO-free acrylic urethane-C (NFAU-C) -- GX-87-3
6. NCO-free acrylic urethane-D (NFAU-D) -- GX-87-37
7. Acrylic urethane-E -- GX-87-44

CATALYST:

DBU -- 1,8-diaza-[5,4,0]-bicycloundecene.

15 NCO-FREE WHITE ACRYLIC ENAMEL FORMULATION:

PART ONE: White Paint-X

Where, X = White Paint-A, White Paint-B or
White Paint-A, and White Paint-B.

- 40 -

PART TWO: Crosslinking Agent-Y

Where, Y = TMPTA, ETMPTA or TMPTA and ETMPTA.

EQ.WT. Ratio of Part One/Part Two = 1/0.8-1

CATALYST: DBU, 0.4-1.0% TRS

5 NCO-FREE WHITE ACRYLIC-URETHANE ENAMEL FORMULATION:**PART ONE: White Paint-X**

Where, X = White Paint-A, White Paint-B or
White Paint-A and White Paint-B.

PART TWO: Crosslinking Agent-Y

10 Where, Y = NFAU-A, NFAU-B, NFAU-C, NFAU-D
 NFAU-E or mixture of both e.g.,
 NFAU-A/NFAU-B, NFAU-D/NFAU-E etc.

EQ.WT. Ratio of Part One/Part Two = 1/0.8-1.0

CATALYST: DBU, 0.4-1.0% TRS

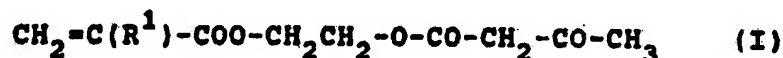
15 Obviously, numerous modifications and variations of
the present invention are possible in light of the above
teachings. It is therefore to be understood that within
the scope of the appended claims, the invention may be
practiced otherwise than as specifically described
20 herein.

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Claims

1. A cured polymer comprising a first component and a second component, wherein said first component comprises at least one acetoacetylated polymer resin and wherein said second component comprises at least one NCO-free urethane polymer having vinylic end groups.

2. The cured polymer of Claim 1, wherein said acetoacetylated (meth)acrylic resin is a copolymer obtained by copolymerizing 10 to 60 wt.% of a monomer of the formula (I)

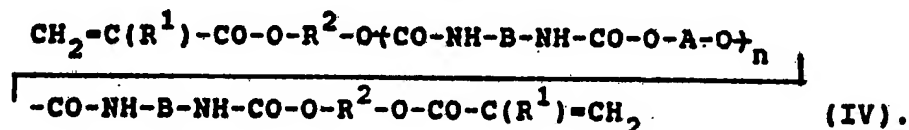


with 90 to 40 wt.% of an alkyl (meth)acrylate of the formula (II)



wherein R is C₁₋₁₂ linear or branched saturated alkyl, and R¹ is H or CH₃.

3. The cured polymer of Claim 2, wherein said NCO-free urethane polymer is a polymer of the formula (IV)



wherein:

each R₁ independently is H or CH₃,

each R₂ independently is a C₂₋₃ linear or branched saturated alkylene moiety;

each B is independently a C₂₋₁₂ linear or branched saturated alkylene moiety, or a C₄₋₁₂ cyclic saturated

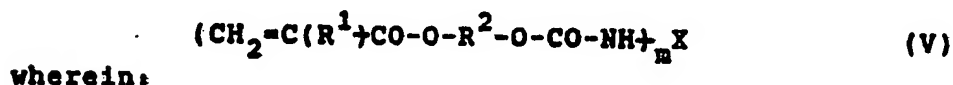
- 42 -

alkylene moiety, or a C₆₋₁₄ arylene moiety;

each A is independently a C₂₋₁₂ linear or branched saturated alkylene moiety, or a C₄₋₁₂ cyclic saturated alkylene moiety, or a C₆₋₁₄ arylene moiety; and

n is an integer of from 1 to 10.

4. The cured polymer of Claim 2, wherein said NCO-free urethane polymer is a polymer of the formula (V):



each R¹ independently is H or CH₃;

Each R² is independently a C₂₋₃ linear or branched saturated alkylene moiety;

X is a C₂₋₁₂ linear or branched saturated alkylene moiety, or a C₄₋₁₂ cyclic saturated alkylene moiety, or a C₆₋₁₄ arylene moiety; and

m is 2, 3 or 4.

5. The cured polymer of Claim 2, wherein said NCO-free urethane polymer is a polymer obtained by:

(1) reacting a reaction mixture of a C₂₋₁₂ linear, branched or cyclic alkyl or aryl polyol having an average of 2 to 4 hydroxyl groups per molecule and a C₂₋₁₄ linear, branched or cyclic saturated alkyl or aryl diisocyanate, triisocyanate, tetraisocyanate, or a mixture thereof, at 5 to 20°C, using a molar ration of OH groups to NCO groups lower than 1.0;

(2) raising the temperature of the mixture of step

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(1) to 40 to 150°C and maintaining said temperature at 40 to 150°C until an NCO content of 4 to 20 wt.% in the reaction mixture is reached;

- 5 (3) adding a hydroxyl substituted alkyl (meth)acrylate of formula (III)



10 wherein:

R^1 is H or CH_3 ; and

15 R^2 is a C_{2-3} linear or branched saturated alkylene moiety; and

maintaining the temperature at 40 to 150°C until the NCO content of the mixture is below 2 wt.%;

- 20 (4) adding to the reaction mixture a C_{1-4} alcohol in an amount appropriate to obtain a ratio of OH groups to NCO groups greater than 1.5; and

- 25 (5) obtaining a NCO-free urethane polymer.

6. The cured polymer of Claim 2, wherein said acetoacetylated (meth)acrylic resin is obtained by reacting said monomer of formula (I) with said alkyl (meth)acrylate of formula (II) and styrene.

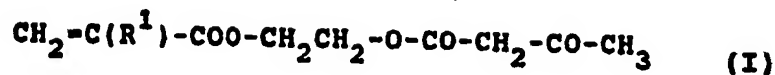
30

7. The cured polymer of Claim 1, further comprising a catalyst having a pKa of 12 to 14.

35 8. The cured polymer of Claim 1, wherein said acetoacetylated polymer is an acetoacetylated polyester obtained by either (1) subjecting an hydroxyl group-containing polyester and a C_{1-4} alkyl acetoacetate to a transesterification reaction, or (2) subjecting an

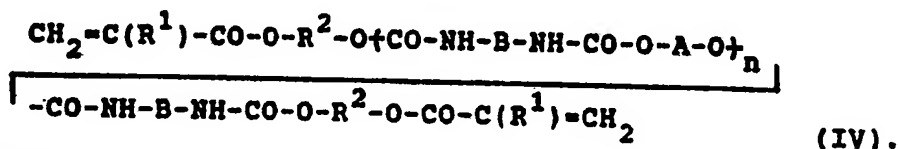
- 44 -

unsaturated polyester and at least one monomer of formula (I)



wherein R^1 is H or CH_3 to a graft polymerization reaction.

9. The cured polymer of Claim 8, wherein said NCO-free urethane polymer is a polymer of the formula (IV)



wherein:

each R^1 independently is H or CH_3 ;

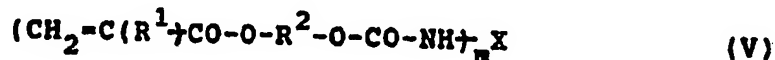
each R^2 independently is a C_{2-3} linear or branched saturated alkylene moiety;

each B is independently a C_{2-12} linear or branched saturated alkylene moiety, or a C_{4-12} cyclic saturated alkylene moiety, or a C_{6-14} arylene moiety;

each A is an independently C_{2-12} linear or branched saturated alkylene moiety, or a C_{4-12} cyclic saturated alkylene moiety, or a C_{6-14} arylene moiety; and

n is an integer of from 1 to 10.

10. The cured polymer of Claim 8, wherein said NCO-free urethane polymer is a polymer of the formula (V):



wherein:

each R^1 independently is H or CH_3 ;

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each R^2 is an independently C_{2-3} linear or branched saturated alkylene moiety;

5 X is a C_{2-12} linear or branched saturated alkylene moiety, or a C_{4-12} cyclic saturated alkylene moiety, or a C_{6-14} arylene moiety; and

m is 2, 3 or 4.

10

11. The cured polymer of Claim 8, wherein said NCO-free urethane polymer is a polymer obtained by:

15 (1) reacting a mixture of a C_{2-12} linear, branched or cyclic alkyl or aryl polyol having an average of 1 to 4 hydroxyl groups per molecule and a C_{2-12} linear, branched or cyclic alkyl or aryl polyol having an average of 1 to 4 hydroxyl groups per molecule and a C_{2-12} linear, branched or cyclic saturated alkyl or aryl diisocyanate, triisocyanate, tetraisocyanate, or mixture thereof, at 5 to 20°C;

20

(2) raising the temperature of the mixture of step (1) to 40 to 150°C and maintaining said temperature at 40 to 150°C with an NCO content of 4 to 20 wt.% in the reaction mixture is reached;

25

(3) adding a hydroxyl substituted alkyl (meth)acrylate of formula (III)

30



wherein:

R-1 is H or CH_3 ; and

35

R^2 is a C_{2-3} linear or branched saturated alkylene moiety; and

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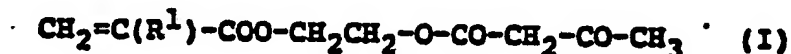
maintaining the temperature at 40 to 150°C until the NCO content of the mixture is below 2 wt.%;

(4) adding to the reaction mixture a C₁₋₄ alcohol in an amount appropriate to obtain a ratio of OH groups to NCO groups greater than 1.5; and

(5) obtaining a NCO-free urethane polymer.

12. An article coated with a coating obtained by curing a first component and a second component, wherein said first component is at least one acetoacetylated polymer resin and wherein said second component is at least one NCO-free urethane polymer having vinylic end groups.

13. The coated article of Claim 12, wherein said acetoacetylated polymer resin is an acetoacetylated(meth)acrylic copolymer resin obtained by copolymerizing 10 to 60 wt.% of a monomer of the formula (I)



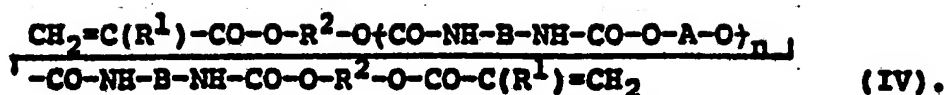
with 90 to 40 wt.% of an alkyl (meth)acrylate of the formula (II)



wherein R is C₁₋₁₂ linear or branched saturated alkyl, and R¹ is H or CH₃.

14. The coated article of Claim 12, wherein said NCO-free urethane polymer is a polymer of the formula (IV)

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wherein:

each R^1 independently is H or CH_3 ;

5 each R^2 independently is a C_{2-3} linear or branched saturated alkylene moiety;

each B is independently a C_{2-12} linear or branched saturated alkylene moiety, or a C_{4-12} cyclic saturated alkylene moiety, or a C_{6-14} arylene moiety;

10 each A is independently a C_{2-12} linear or branched saturated alkylene moiety, or a C_{4-12} cyclic saturated alkylene moiety, or a C_{6-14} arylene moiety; and

n is an integer of from 1 to 10.

15 15. The coated article of Claim 12, wherein said NCO-free urethane polymer is a polymer of the formula (V):



wherein:

each R^1 independently is H or CH_3 ;

20 each R^2 is independently a C_{2-3} linear or branched saturated alkylene moiety;

X is a C_{2-12} linear or branched saturated alkylene moiety, or a C_{4-12} cyclic saturated alkylene moiety, or a C_{6-14} arylene moiety; and

25 m is 2, 3 or 4.

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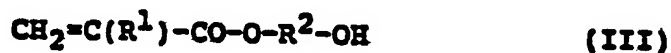
- 48 -

16. The coated article of Claim 12, wherein said NCO-free urethane polymer is a polymer obtained by:

(1) reacting a mixture of a C₂₋₁₂ linear, branched or cyclic alkyl or aryl polyol having an average of 2 to 4 hydroxyl groups per molecule and a C₂₋₁₂ linear, branched or cyclic saturated alkyl or aryl diisocyanate, triisocyanate, tetraisocyanate, or a mixture thereof, at 5 to 20°C, using a molar ratio of OH groups to NCO groups lower than 1.0

(2) raising the temperature of the mixture of step (1) to 40 to 150°C and maintaining said temperature at 40 to 150°C with an NCO content of 4 to 20 wt.% in the reaction mixture is reached;

(3) adding a hydroxyl substituted alkyl (meth)acrylate of formula (III)



wherein:

R¹ is H or CH₃; and

R² is a C₂₋₃ linear or branched saturated alkylene moiety; and

maintaining the temperature at 40 to 150°C until the NCO content of the mixture is below 2 wt.%;

(4) adding to the reaction mixture a C₁₋₄ alcohol in an amount appropriate to obtain a ratio of OH groups to NCO groups greater than 1.5; and

(5) obtaining a NCO-free urethane polymer.

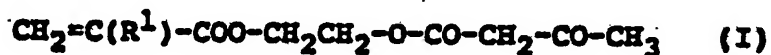
17. The coated article of Claim 13, wherein said

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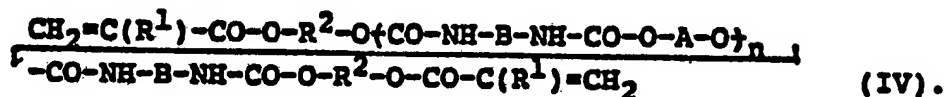
acetoacetylated (meth)acrylic resin is obtained by reacting said monomer of formula (I) with said alkyl (meth)acrylate of formula (II) and styrene.

18. The coated article of Claim 12, wherein said
5 acetoacetylated polymer is acetoacetylated polyester obtained by either (1) subjecting a hydroxy group-containing polyester and a C₁₋₄ alkylacetoacetate to a transesterification reaction, or (2) subjecting an
10 unsaturated polyester and at least one monomer of formula (I)



wherein R¹ is H or CH₃ to a graft polymerization reaction.

19. The coated article of Claim 18, wherein said
15 NCO-free urethane polymer is a polymer of the formula (IV)



wherein:

20 each R¹ independently is H or CH₃;

each R² independently is a C₂₋₃ linear or branched saturated alkylene moiety;

each B is independently a C₂₋₁₂ linear or branched saturated alkylene moiety, or a C₄₋₁₂ cyclic saturated
25 alkylene moiety, or a C₆₋₁₄ arylene moiety;

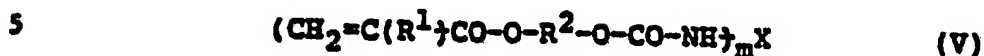
each A is independently a C₂₋₁₂ linear or branched saturated alkylene moiety, or a C₄₋₁₂ cyclic saturated alkylene moiety, or a C₆₋₁₂ arylene moiety; and

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n is an integer of from 1 to 10.

20. The coated article of Claim 18, wherein said NCO-free urethane polymer is a polymer of the formula (V):



wherein:

each R^1 independently is H or CH_3 ;

each R^2 is independently a C_{2-3} linear or branched saturated alkylene moiety;

10 X is a C_{2-12} linear or branched saturated alkylene moiety, or a C_{4-12} cyclic saturated alkylene moiety, or a C_{6-14} arylene moiety; and

m is 2, 3 or 4.

21. The coated article of Claim 12, wherein said
15 NCO-free urethane polymer is a polymer obtained by:

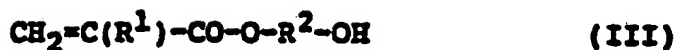
(1) reacting a reaction mixture of a C_{2-12} linear, branched or cyclic alkyl or aryl polyol having an average of 2 to 4 hydroxyl groups per molecule and a C_{2-12} linear, branched or cyclic saturated alkyl or aryl
20 diisocyanate, triisocyanate, tetraisocyanate, or mixture thereof, at 5 to 20°C ;

(2) raising the temperature of the mixture of step (1) to 40 to 150°C and maintaining said temperature at 40 to 150°C with an NCO content of 4 to 20 wt.% in the
25 reaction mixture reached;

(3) adding a hydroxyl substituted alkyl (meth)acrylate of formula (III)

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wherein:

R^1 is H or CH_3 ; and

R^2 is a C_{2-3} linear or branched saturated alkylene moiety; and

maintaining the temperature at 40 to 150°C until the NCO content of the mixture is below 2 wt.%;

(4) adding to the reaction mixture a C_{1-4} alcohol in an amount appropriate to obtain a ratio of OH groups to NCO groups greater than 1.5; and

(5) obtaining a NCO-free urethane polymer.

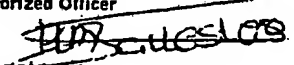
22. An article obtained by curing a first component and a second component, wherein said first component comprises at least one an acetoacetylated polymer resin and wherein said second component comprises at least one NCO-free urethane polymer having vinylic end groups.

23. The article of Claim 22, wherein said article is an automobile, a fabric-based article or a shoe.

24. A double pane window, comprising two panes of glass bound to each other with an adhesive composition obtained by curing at least one acetoacetylated polymer resin with at least one NCO-free urethane polymer having vinylic end groups.

INTERNATIONAL SEARCH REPORT

International Application No PCT/CA 90/00006

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 08 L 67/07, 75/16, C 09 D 167/07, 175/16						
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 25%; border-bottom: 1px solid black;">Classification System</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="height: 40px; vertical-align: bottom;">IPC5</td> <td style="vertical-align: bottom;">C 08 L; C 09 D</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div>			Classification System	Classification Symbols	IPC5	C 08 L; C 09 D
Classification System	Classification Symbols					
IPC5	C 08 L; C 09 D					
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹:						
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³				
A	STN International, File CA, Chemical Abstracts, volume 93, no. 8, 25 August 1980, (Columbus, Ohio, US), Nippon Synthetic Chemical Industry Co., Ltd., Japan): "Rosin compositions", abstract 73909h, & Jpn. Kokai Tokkyo Koho JP 55040711 22 Mar 1980 Showa, 12 pp. (Japan)	1-22				
--						
A	Dialog Information Services, File 351, World Patent Index 81-90, Dialog accession no. 81-18601D/11, Nippon Synth Chem Ind: "Resin compsn. forming water, alkali and solvent-resistant coating comprises acetoacetyl gp.-contg. polyester and amino resin; AMINOPLAST", JP 56005847, A, 810121, 8111 (Basic)	1-22				
--						
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>						
IV. CERTIFICATION						
Date of the Actual Completion of the International Search 29th August 1990	Date of Mailing of this International Search Report 28. 09. 90					
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer <div style="text-align: center;">  H. Ballesteros </div>					

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	STN International, File CA, Chemical Abstracts, volume 112, no. 4, 22 January 1990, (Columbus, Ohio, US), Del Rector F: "A comparison of methods for the preparation of acetoacetylated coating resins", abstract 22391m, & Proc. Water-Borne Higher-Solids Coat. Symp., 16th, 400-27 (Eng) --	2,6,8, 17-18
A	EP, A2, 0366884 (AMERICAN CYANAMID COMPANY) 9 May 1990, see the whole document -- -----	1-22

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/CA 90/00006**

SA 33352

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on **02/08/90**
The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0366884	09/05/90	NONE	

For more details about this annex : see Official Journal of the European patent Office, No. 12/82